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Natural Phenolic Adhesives I: Tannin

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I. INTRODUCTION

The loose term *renewable resources adhesives* has been used to identify polymeric compounds of natural, vegetable origin that have been modified and/or adapted to the same use as some classes of purely synthetic adhesives [1]. At present two classes of these adhesives exist: one already extensively commercialized in the southern hemisphere and the other on the slow way to commercialization. These two types of resins are tannin-based adhesives [2] and lignin adhesives [3–6]. Both types are aimed primarily at substituting synthetic phenolic resins. In some aspects, such as performance, they closely mimic, or are even superior to, synthetic phenolic adhesives, while in others they behave in a vastly different manner from their synthetic counterparts. In this chapter we focus primarily on tannin-based adhesives because they have already been in extensive industrial use in the southern hemisphere, in certain fields of application, for the past 20 years. These adhesives are of some interest not only for their excellent performance in some applications but also for their mostly environmentally friendly composition. Lignin adhesives are treated briefly here and in detail in Chap. 28.

II. LIGNIN ADHESIVES

Lignin is a phenolic polymer that is one of the main polymeric constituents of wood formula (1). It is generally produced in great quantities as waste from paper pulp mills. It is composed of repeating phenylpropane units. Considerable research has been carried out on lignin adhesives and binders. While for certain applications, such as binders for nontarred rough rural roads, lignin derivatives have been used for many years, in the main area of potential application—wood adhesives—industrial use has been lagging. A variety of effective lignin adhesive formulations exist and have already been reviewed extensively [3], some of them having been used for some length of time in some particleboard or plywood mills. Not all these formulations are used today because all of them always come up against two broad problems: the formulation tends to be corrosive or hard on equipment in the plant, or the lignin in the formulation tends to noticeably slow down panel pressing time, with consequent loss of mill productivity. In North America there are now

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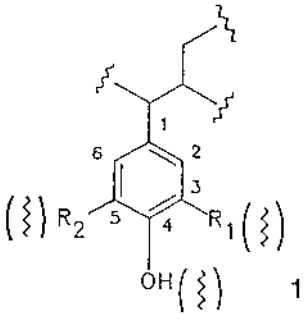
encouraging indications that premethylolated lignin (prereacted with formaldehyde) can be added in place of up to 20 to 30% of synthetic phenolic resins for plywood without lengthening panel pressing times, and a few mills already appear to have been using such a system for some time [4]. Recent claims that industrial use of wood adhesive formulations containing up to 50% lignin has occurred for some years but has now been discontinued purely on economical grounds have proven to be true and reliable [7]. Considering their very limited application, the reader is referred to more extensive reviews on this subject [3,6].



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III. TANNIN-BASED ADHESIVES

The word tannin has been used loosely to define two different classes of chemical compounds of mainly phenolic nature: hydrolyzable tannins and condensed tannins. The former, including chestnut, myrabalans (*Terminalia* and *Phyllantus* tree species), and divi-divi (*Caesalpina coriaria*) extracts, are mixtures of simple phenols such as pyrogallol and ellagic acid and of esters of a sugar, mainly glucose, with gallic and digallic acids [2]. They can and have been used successfully as partial substitutes (up to 50%) for phenol in the manufacture of phenol–formaldehyde resins [8,9]. Their chemical behavior towards formaldehyde is analogous to that of simple phenols of low reactivity and their moderate use as phenol substitutes in the above-mentioned resins does not present difficulties. Their lack of macromolecular structure in their natural state, the low level of phenol substitution they allow, their low nucleophilicity, limited worldwide production, and their higher price somewhat decrease their chemical and economical interest.

Condensed tannins, on the other hand, constituting more than 90% of the total world production of commercial tannins (200,000 tons per year), are both chemically and economically more interesting for the preparation of adhesives and resins. Condensed tannins and their flavonoid precursors are known for their wide distribution in nature and particularly for their substantial concentration in the wood and bark of various trees. These include various *Acacia* (wattle or mimosa bark extract), *Schinopsis* (quebracho wood extract), *Tsuga* (hemlock bark extract), and *Rhus* (sumach extract) species, from which commercial tannin extracts are manufactured, and various *Pinus* bark extract species. Where the bark and wood of trees were found to be particularly rich sources of condensed tannins, commercial development ensued through large-scale afforestation and/or industrial extraction, mainly for use in leather tanning. The production of tannins for leather manufacture reached its peak immediately after World War II and has since progressively declined. This decline of their traditional market, coupled with the increased price and decreased availability of synthetic phenolic

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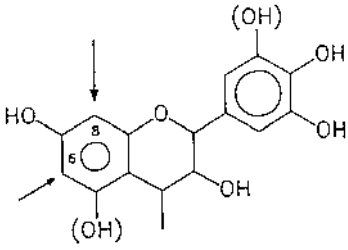
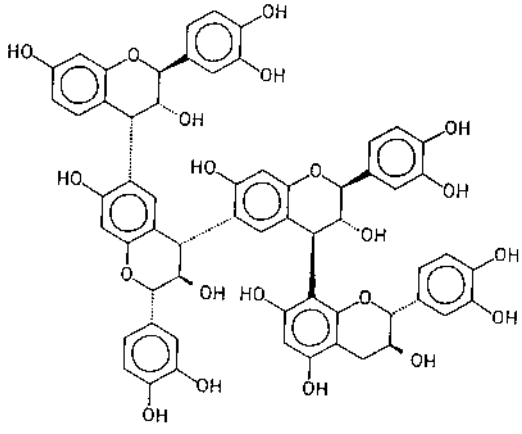
materials due to the advent of the energy crisis of the early 1970s, stimulated fundamental and applied research on the use of such tannins as a source of condensed phenolics.

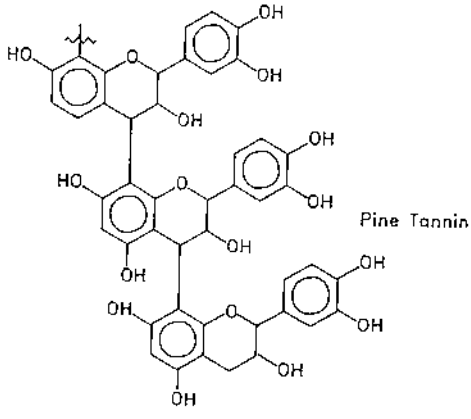
A. Condensed Tannins

The structure of the flavonoid constituting the main monomer of condensed tannins may be represented as follows:



this flavonoid unit is repeated 2 to 11 times in mimosa tannin, with an average degree of polymerization of 4 to 5, and up to 30 times for pine tannins, with an average degree of polymerization of 6 to 7 for their soluble extract fraction [10–12].





The nucleophilic centers on the A ring of a flavonoid unit tend to be more reactive than those found on the B ring. This is due to the vicinal hydroxyl substituents, which cause general activation in the B ring without any localized effects such as those found in the A ring.

Formaldehyde reacts with tannins to produce polymerization through methylene bridge linkages at reactive positions on the flavonoid molecules, mainly the A rings. The reactive positions of the A rings are one of positions 6 or 8 (according to the type of tannin) of all the flavonoid units and both positions 6 and 8 of the upper terminal flavonoid units. The A rings of mimosa and quebracho tannins show reactivity toward formaldehyde comparable to that of resorcinol [13–15]. Assuming the reactivity of phenol to be 1 and that of resorcinol to be 10, the A rings have a reactivity of 8 to 9. However, because of their size and shape, the tannin molecules become immobile at a low level of

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condensation with formaldehyde, so that the available reactive sites are too far apart for further methylene bridge formation. The result may be incomplete polymerization and therefore weakness. Bridging agents with longer molecules should be capable of bridging the distances that are too long for methylene bridges. Alternatively, other techniques can be used to solve this problem.

In condensed tannins from mimosa bark the main polyphenolic pattern is represented by flavonoid analogs based on resorcinol A rings and pyrogallol B rings. These constitute about 70% of the tannins. The secondary but parallel pattern is based on resorcinol A rings and catechol B rings [2,14]. These tannins represent about 25% of the total of the mimosa bark tannin fraction. The remaining part of the condensed tannin extract is the "nontannins" [14]. They may be subdivided into carbohydrates, hydrocolloid gums, and small amino and imino acid fractions [2,14]. The hydrocolloid gums vary in concentration from 3 to 6% and contribute significantly to the viscosity of the extract despite their low concentration [2,14]. Similar flavonoid A- and B-ring patterns also exist in quebracho wood extract (*Schinopsis balansae* and *Schinopsis lorentzii*) [13–15], but no phloroglucinol A-ring pattern, or probably a much lower quantity of it, exists in quebracho extract [15–17]. Similar patterns to wattle (mimosa) and quebracho are followed by hemlock and Douglas fir bark extracts. Completely different patterns and relationships do instead exist in the case of pine tannins [18–20] which present instead only two main patterns: one represented by flavonoid analogs based on phloroglucinol A rings and catechol B rings [18,20]. The other pattern, present in much lower proportion, is represented by phloroglucinol A rings and phenol B rings [18,20]. The A rings of pine tannins then possess only the phloroglucinol type of structure, much more reactive toward formaldehyde than a resorcinol-type structure, with important consequences in the use of these tannins for adhesives.

In condensed polyflavonoid tannin molecules the A rings of the constituent flavonoid units retain only one highly reactive nucleophilic center, the remainder accommodating the interflavonoid bonds. Resorcinolic A rings (wattle) show reactivity toward formaldehyde comparable to, though slightly lower than that of resorcinol [21]. Phloroglucinolic A rings (pine) behave instead as phloroglucinol [22]. Pyrogallol or catechol B rings are by comparison unreactive and may be activated by anion formation only at relatively high pH [16]. Hence the B rings do not participate in the reaction except at high pH values (pH 10), where the reactivity toward formaldehyde of the A rings is so high that the tannin–formaldehyde adhesives prepared have unacceptably short pot lives [21]. In general tannin adhesive practice, only the A rings are used to cross-link the network. With regard to the pH dependence of the reaction with formaldehyde, it is generally accepted that the reaction rate of wattle tannins with formaldehyde is slowest in the pH range 4.0 to 4.5 [23]; for pine tannins, the range is between 3.3 and 3.9.

Formaldehyde is generally the aldehyde used in the preparation, setting, and curing of tannin adhesives. It is normally added to the tannin extract solution at the required pH, preferably in its polymeric form of paraformaldehyde, which is capable of fairly rapid depolymerization under alkaline conditions, and as urea–formalin concentrates. Hexamethylenetetramine (hexamine) may also be added to resins due to its potential formaldehyde releasing action under heat. Hexamine is, however, unstable in acid media [24] but becomes more stable with increased pH values. Hence under alkaline conditions the liberation of formaldehyde might not be as rapid and as efficient as wanted. Also, it has been fairly widely reported, with a few notable exceptions [25], that bonds formed with hexamine as hardener are not as boil resistant [26] as those formed by paraformaldehyde. The reaction of formaldehyde with tannins may be controlled by the

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addition of alcohols to the system. Under these circumstances some of the formaldehyde is stabilized by the formation of hemiacetals [e.g., $CH_2(OH)(OCH_3)$] if methanol is used [2,22]. When the adhesive is cured at an elevated temperature, the alcohol is driven off at a fairly constant rate and formaldehyde is progressively released from the hemiacetal. This ensures that less formaldehyde is volatilized when the reactants reach curing temperature and that the pot life of the adhesive is extended. Other aldehydes have also been substituted for formaldehyde [2,21,23,25].

In the reaction of polyflavonoid tannins with formaldehyde two competitive reactions are present:

1. The reaction of the aldehyde with tannin and with low-molecular-weight tannin–aldehyde condensates, which are responsible for the aldehyde consumption.
2. The liberation of aldehyde, available again for reaction. This reaction is probably due to the passage of unstable $–CH_2–O–CH_2–$ ether bridges initially formed to $–CH_2–$ linked compounds.

In the case of some tannins, namely quebracho tannin, a third reaction of importance is present,

3. The simultaneous hydrolysis of some interflavonoid bonds, hence a depolymerization reaction, partly counteracting and hence slowing down hardening [26–28]. Notwithstanding that the two major industrial polyflavonoid tannins which exist, namely mimosa and quebracho tannins, are very similar and both composed of mixed prorobinetinidins and profisetinidins one could not explain this anomalous behavior of quebracho tannin. It has now been possible to determine by both nuclear magnetic resonance (NMR) [26] and particularly by laser desorption mass spectrometry (MALDI-TOF) for mimosa and quebracho tannins and some of their modified derivatives [28] that: (i) mimosa tannin is predominantly composed of prorobinetinidins while quebracho is predominantly composed of profisetinidins, (ii) mimosa tannin is heavily branched due to the presence of considerable proportions of ''angular'' units in its structure while quebracho tannin is almost completely linear [28]. This latter structural difference contributes to the considerable differences in viscosity of water solutions of the two tannins and which (iii) induces the interflavonoid link of quebracho to be more easily hydrolyzable, due to the linear structure of this tannin, confirming NMR findings [26,28] that this tannin is subject to polymerization/depolymerization equilibria. This also showed that the decrease of viscosity due to acid/base treatments to yield tannin adhesive intermediates does also depend in quebracho on a certain level of hydrolysis of the tannin itself and not only of the carbohydrates present in the extract (see Section IV). This tannin hydrolysis does not appear to occur in mimosa tannin in which the interflavonoid link is completely stable to hydrolysis.

It is interesting to note that while $–CH_2–O–CH_2–$ ether bridged compounds have been isolated for the phenol–formaldehyde [24] reaction, their existence for fast-reacting phenols such as resorcinol and phloroglucinol has been postulated, but they have not been isolated, as these two phenols have always been considered too reactive with formaldehyde. They are detected by a surge in the concentration of formaldehyde observed in kinetic curves due to methylene ether bridge decomposition [19].

When heated in the presence of strong mineral acids, condensed tannins are subject to two competitive reactions. One is degradative leading to lower-molecular-weight products, and the second is condensative as a result of hydrolysis of heterocyclic rings (*p*-hydroxybenzyl ether links) [16]. The *p*-hydroxybenzylcarbonium ions created condense randomly with nucleophilic centers on other tannin units to form ''phlobaphenes'' or

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''tanner's red'' [16,29–31]. Other modes of condensation (e.g. free radical coupling of B-ring catechol units) cannot be excluded in the presence of atmospheric oxygen. In predominantly aqueous conditions, phlobaphene formation or formation of insoluble condensates predominates. These reactions, characteristic of tannins and not of synthetic phenolic resins, must be taken into account when formulating tannin adhesives.

Sulfitation of tannin in one of the oldest and most useful reactions in flavonoid chemistry. Slightly sulfited water is sometimes used to increase tannin extraction from the bark containing it. In certain types of adhesives, the total effect of sulfitation, while affording the important advantages of higher concentration of tannin phenolics in adhesive applications due to enhanced solubility and decreased viscosity, and of higher moisture retention by the tannin resins, allowing slower adhesive film dry-out, hence longer assembly times [32], also represents a distinct disadvantage in that sulfonate groups promote sensitivity to moisture with adhesive deterioration and poor water resistance of the cured glue line even with adequate cross-linking [32–35].

In recent years the importance of the marked colloidal nature of tannin extract solutions has come to the fore [27,36–45]. It is the presence of both polymeric carbohydrates in the extract as well as of the higher molecular fraction of the polyphenolic tannins which determines the colloidal state of tannin extract solutions in water [26,36]. The realization of the existence of the tannin in this particular state affects many of the reactions that lead to the formation and curing of tannin adhesives, to the point that reactions not thought possible in solution become instead not only possible but the favored ones [26,36], while reactions mooted to be of determinant importance when found on models not in the colloidal state have in reality been shown to be inconsequential to tannin adhesives and their tannin applications [43,44].

IV. TECHNOLOGY OF INDUSTRIAL TANNIN ADHESIVES

The purity of vegetable tannin extracts varies considerably. Commercial wattle bark extracts normally contain 70 to 80% active phenolic ingredients. The nontannin fraction, consisting mainly of simple sugars and high-molecular-weight hydrocolloid gums, does not participate in the resin formation with formaldehyde. Sugars reduce the strength and water resistance in direct proportion to the amount added. Their effect is a mere dilution of the adhesive resin solids, with consequent proportional worsening of adhesive properties. The hydrocolloid gums, instead, have a much more marked effect on both original strength and water resistance of the adhesive [2,22,42]. If it is assumed that the nontannins in tannin extracts have a similar influence on adhesive properties, it can expected that unfortified tannin–formaldehyde networks can achieve only 70 to 80% of the performance shown by synthetic adhesives. In many glued wood products, the demands on the glue line are so high that unmodified tannin adhesives are unsuitable. The possibility of refining extracts has proved fruitless largely because the intimate association between the various constituents makes industrial fractionation difficult. Fortification is in many cases the most practical approach to reducing the effect of impurities. Fortification generally consists of copolymerization of the tannin with phenolic or aminoplastic resins [21,22,42,46]. It can be carried out during manufacture of the adhesive resin, during glue mix assembly, just before use, or during adhesive use. If added in sufficient quantity, various synthetic resins have been found effective in reducing the nontannin fraction to below 20% and in overcoming other structural problems [21,22]. The main resins used are phenol–formaldehyde and urea–formaldehyde resols with a medium to high methylol group content. These

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resins can fulfill the functions of hardeners, fortifiers, or both. Generally, they are used as fortifiers in between 10 and 20% of total adhesive solids, and paraformaldehyde is used as a hardener. Such an approach is the favorite one for marine-grade plywood adhesives. These fortifiers are particularly suitable for the resorcinolic types of condensed tannins, such as mimosa. They can be copolymerized with the tannins during resin manufacture, during use, or both [2,21,22,42,44]. Copolymerization and curing are based on the condensation of the tannin with the methylol groups carried by the synthetic resin. Since tannin molecules are generally large, the rate of molecular growth in relation to the rate of linkage is high, so that tannin adhesives generally tend to have fast gelling and curing times and shorter pot lives than those of synthetic phenolic adhesives. From the point of view of reactivity, phloroglucinol tannins such as pine tannins are much faster than mainly resorcinol tannins such as mimosa. The usual ways of slowing them down and, for instance, of lengthening adhesive pot life are:

1. To add alcohols to the adhesive mix to form hemiacetals with formaldehyde and therefore act as retardants of the tannin–formaldehyde reaction.
2. To adjust the adhesive's pH to have the required pot life and rate of curing.
3. To use hexamine as a hardener, which under the current conditions gives a very long pot life at ambient temperature but still fast curing time at higher temperatures.

The viscosity of bark extracts is strongly dependent on concentration. The viscosity increases very rapidly above a concentration of 50%. Compared to synthetic resins, tannin extracts are more viscous at the concentrations normally required in adhesives. The high viscosity of aqueous solutions of condensed tannins is due to the following causes, in order of importance:

1. *Presence of high-molecular-weight hydrocolloid gums in the tannin extract* [42,45]. The viscosity is directly proportional to the amount of gums present in the extract [42,45].
2. *Tannin–tannin*, *tannin–gum*, *and gum–gum hydrogen bonds*. Aqueous tannin extract solutions are not true solutions but, rather, colloidal suspensions in which water access to all parts of the molecules present is very slow. As a consequence, it is difficult to eliminate intermolecular hydrogen bonds by dilution only [42,45].
3. *Presence of high-molecular-weight tannins in the extract* [28,42,45].

The high viscosity of tannin extract solutions has also been correlated with the proportion of very-high-molecular-weight tannins present in the extract. This effect is not well defined. In most adhesive applications such as in plywood adhesives, the viscosity is not critical and can be manipulated by dilution.

In the case of particleboard adhesives decrease of viscosity is, instead, an important prerequisite. When reacted with formaldehyde, unmodified condensed tannins give adhesives having characteristics that do not suit particleboard manufacture: namely, high viscosity, low strength, and poor water resistance. The most commonly used process to eliminate these disadvantages in the preparation of tannin-based particleboard adhesives consists of a series of subsequent acid and alkaline treatments of the tannin extract, causing hydrolysis of the gums to simple sugars and some tannin structural changes, thus improving the viscosity, strength, and water resistance of the unfortified tannin–formaldehyde adhesive [2,44]. Furthermore, such treatments may cause partial rearrangement of the flavonoid molecules that causes liberation of some resorcinol in

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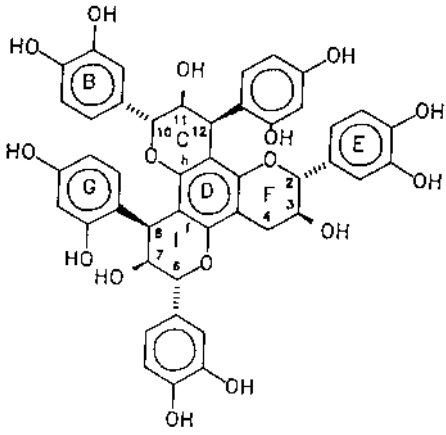
situ in the tannin, rendering it more reactive, allowing better cross-linking with formaldehyde, and ultimately yielding an adhesive which without addition of any fortifier resins gives truly excellent performance for exterior-grade particleboard [1,2,44]. Such rearranged "phlobatannin" structures have formula as follows:



This modification cannot be carried out too extensively, but only to a limited extent to avoid precipitation of the tannin from solution by the formation of "phlobaphenes." Typical results obtained are shown in Table 1.

Particular gluing and pressing techniques have been developed for tannin particleboard adhesives [47,48] to achieve pressing times much faster than those traditionally obtained with synthetic phenol–formaldehyde adhesives, although recent advances in synthetic phenol–formaldehyde resins have markedly limited such an advantage [49,50]. Pressing times of 7 s/mm of panel thickness have been achieved and pressing times of 9 s/mm at 190 to 200°C press temperature are in daily operation: these are pressing times comparable to what is obtainable with urea–formaldehyde or melamine–formaldehyde resins at the same pressing temperatures. The success of these simple types of particleboard adhesives relies heavily on industrial application technology rather than just on the preparation technology of the adhesive itself [42,47,51]. A considerable advantage is the much higher moisture content of the resinated chips tolerable with these adhesives than with any of the synthetic phenolic and amino resin adhesives. In the case of wood particleboard and of oriented strandboard (OSB) panels the technology so developed allows hot pressing at moisture contents of around 24% against values of 12% for traditional synthetic adhesives, and presents other advantages as well [42,51,52].

Table 1 Unfortified Tannin–Formaldehyde Adhesives Obtained by Acid–Alkali Treatment for Exterior-Grade Particleboard: Example of Industrial Board Results

	Swelling after a 2-h boil				
Panel density (g/cm^3)	Measured wet (%)	Measured dry (irreversible swelling) (%)	Original IB, tensile perpendicular (kg/cm^2)	IB after a 2-h boil (kg/cm^2)	Cyclic test after five cycles measured (%)
0.700	11.0	0.0	13.0	9.0	3.0

IB, internal bond.

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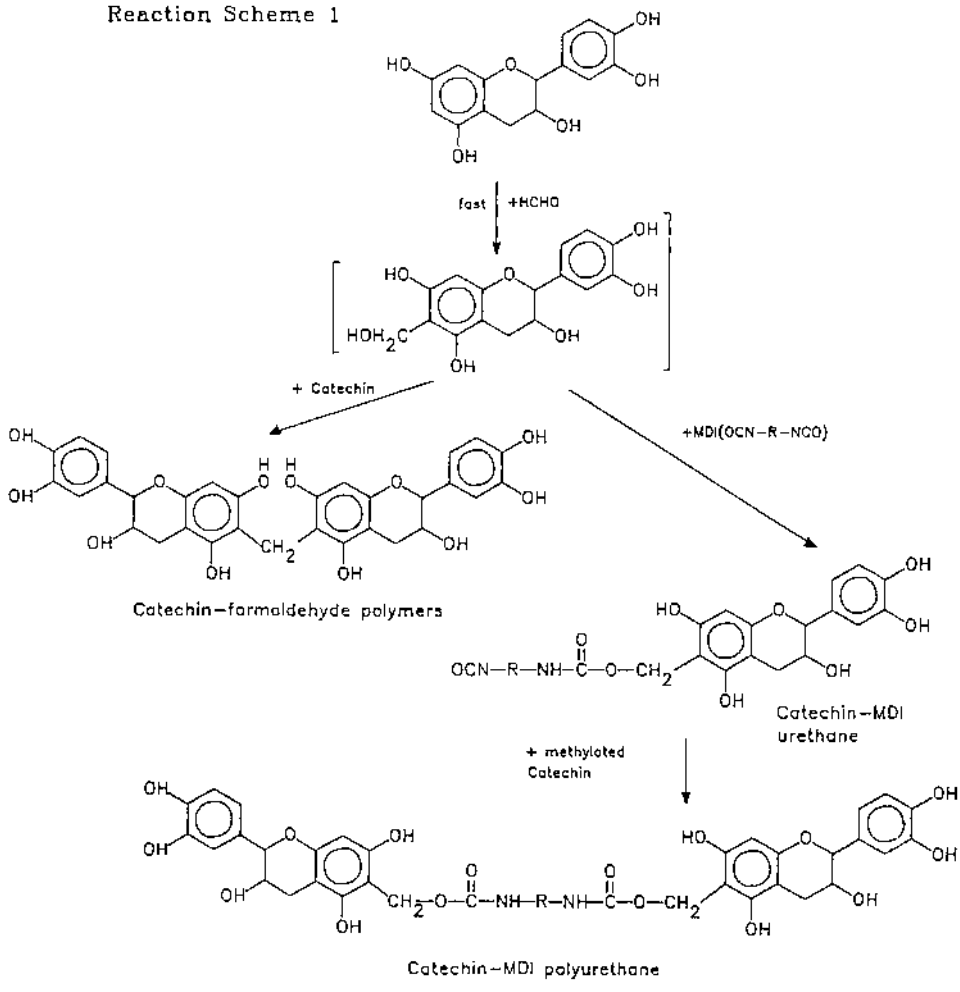
The best adhesive formulation for phloroglucinolic tannins such as pine tannin extracts is, instead, a comparatively new adhesive formulation that is also capable of giving excellent results when using resorcinolic tannins such as a wattle tannin extract [53–56]. The adhesive glue mix consists only of a mix of an unmodified tannin extract in 50% solution to which has been added paraformaldehyde and polymeric nonemulsifiable 4,4′-diphenylmethane diisocyanate (commercial pMDI) [53–56]. The proportion of tannin extract solids to pMDI can be as high as 70:30 based on mass, but can be much lower in pMDI content. This adhesive is based on the following peculiar mechanism, by which the MDI, in water, is hardly deactivated to polyureas [54,56]:



The properties of the particleboard manufactured with this system using pine tannin adhesives are listed in Table 2. The results obtainable with this system are then quite good and not too different from the results obtainable with some of the other tannin adhesives already described. In the case of phloroglucinolic tannin extracts being used, no pH adjustment of the solution is needed. One point that was given close consideration is the deactivating effect of water on the isocyanate group of pMDI. It has been found

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Table 2 Properties of Particleboard Manufactured Using Pine Tannin Adhesives

Panel density (g/cm^3)	Swelling after a 2-h boil: Measured wet (%)	Swelling after a 2-h boil: Measured dry (irreversible swelling) (%)	Original IB, tensile perpendicular (kg/cm^2)	IB after a 2-h boil (kg/cm^2)	IB retention after a 2-h boil (%)
0.690	15.0	4.3	8.4	4.3	51

IB, internal bond.

that the amount of deactivation by water of this group when in a concentrated solution (50% or over) of a phenol is much lower than previously thought [53–56]. This is the reason that aqueous tannin extract solutions and pMDI can be reacted without substantial pMDI deactivation by the water present.

The quest to decrease or completely eliminate formaldehyde emission from wood panels bonded with adhesives, although not really necessary in tannin adhesives due to their very low emission (as most phenolic adhesives), has nonetheless promoted some research to further improve formaldehyde emission. This has centered on two lines of investigation: (i) autocondensation of tannins (see Section IV. D below), and (ii) the use of hardeners that do not emit at all simply because no aldehyde has been added to the tannin. Methylolated nitroparaffins and in particular the simpler and least expensive exponent of their class, namely trishydroxymethyl nitromethane [57,58], function well as hardeners of a variety of tannin-based adhesives while affording considerable side advantages to the adhesive and to the bonded wood joint. In panel products such as particleboard, medium density fiberboard (MDF), and plywood the joint performance that is obtained is of the exterior/marine grade type, while a very advantageous considerable lengthening in glue mix pot life is obtained. Furthermore, the use of this hardener is coupled with such a marked reduction in formaldehyde emission from the bonded wood panel as to reduce emission exclusively to the formaldehyde emitted by heating just the wood (and slightly less, thus functioning as a mild depressant of emission from the wood itself). Furthermore, trishydroxymethyl nitromethane can be mixed in any proportion with traditional formaldehyde-based hardeners for tannin adhesives, its proportional substitution of such hardeners inducing a proportionally marked decrease in the formaldehyde emission of the wood panel without affecting the exterior/marine grade performance of the panel. Medium density fiberboard industrial plant trials confirmed all the properties reported above and the trial conditions and results are reported [57,58]. A cheaper but as equally effective alternative to hydroxymethylated nitroparaffins is the use of hexamine as a tannin hardener. This sometimes causes problems of early agglomeration in some tannins [59] and a better solution proposed which overcame such problems was rather to use as a hardener a mix of formaldehyde coupled with an ammonium salt.

A. Corrugated Cardboard Adhesives

The adhesive developed for the manufacture of damp-ply-resistant corrugated cardboard are based on the addition of spray-dried wattle extract, urea–formaldehyde resin, and formaldehyde to a typical Stein–Hall starch formula of 18 to 22% starch content [60,61]. The wattle tannin–urea–formaldehyde copolymer formed in situ, and any free

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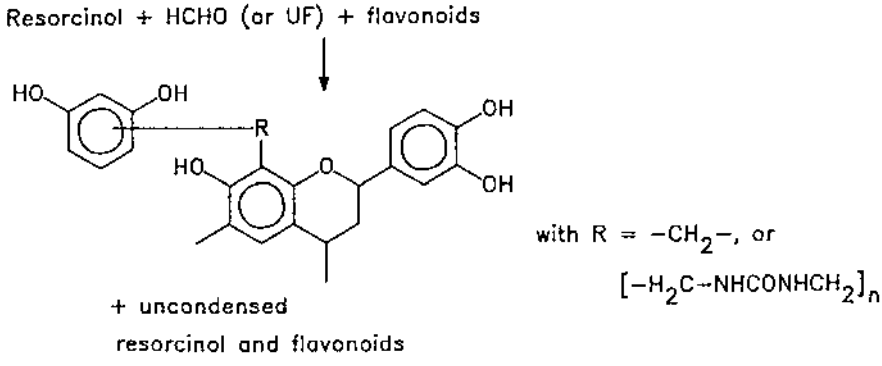
formaldehyde left in the glue line is absorbed by the wattle tannin extract. The wattle extract powder should be added at a level of 4 to 5% of the total starch content of the mix (i.e., carrier plus slurry). Successful results can be achieved in the range of 2 to 12% of the total starch content, but 4% is the recommended starting level. The final level is determined by the degree of water hardness and desired bond quality. This wattle extract–urea–formaldehyde fortifier system is highly flexible and can be adopted to dampproof a multitude of basic starch formulations.

B. Cold-Setting Laminating and Fingerjointing Adhesives for Wood

A series of different novolak-like materials are prepared by copolymerization of resorcinol with resorcinolic A rings of polyflavonoids, such as condensed tannins [62–64]. The copolymers formed have been used as cold-setting exterior-grade wood adhesives, complying with the relevant international specifications. Several formulations are used. The system most commonly used commercially relies on the simultaneous copolymerization of resorcinol and of the resorcinolic A rings of the tannin, due to their comparable reactivities toward formaldehyde.



The final mixture of the products of this system is an adhesive that can be set and cured at ambient temperature by the addition of paraformaldehyde. Other cold-set systems exist and are described in the more specialized literature [2,62–64]. The typical results obtainable with these adhesives are indicated in Table 3.

A particularly interesting system now used extensively in several southern hemisphere countries is the so-called ''honeymoon'' fast-setting, separate-application system [66,67]. In this system one of the surfaces to be mated in the joint is spread with a standard synthetic phenol–resorcinol–formaldehyde adhesive plus paraformaldehyde hardener. The second surface is spread with a 50% tannin solution at pH 12. When the two surfaces are

Table 3 Typical Results of Tannin–Resorcinol–Formaldehyde Cold-Setting Adhesives used on Beech Strips according to British Standard BS 1204 [65]

	Dry	After a 24-h cold-water soak	After a 6-h boil
Tensile strength (N)	3200–3800	2300–2900	2200–2800
Wood failure (%)	90–100	75–100	80–100

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jointed, fingerjoints develop enough strength to be installed within 30 min and laminated beams (glulam) need to be clamped for only 2.5 to 3 h instead of the traditional 16 to 24 h, with a consequent considerable increase of factory productivity. This adhesive system also provides full weather- and boil-proof capabilities.

C. Tire Cord Adhesives

Another application of condensed tannin extracts that has proved technically successful is as tire cord adhesives. Both thermosetting tannin formulations [68] and tannin–resorcinol–formaldehyde formulations have been experimented with successfully.

D. New Concepts and Principles

1. *Surface Catalysis*

As in the case of other formaldehyde-based resins the interaction energies of tannins with cellulose obtained by molecular mechanics calculations [43] tend to confirm the effect of surface catalysis induced by cellulose on the curing and hardening reaction of tannin adhesives. The considerable energies of interactions obtained can effectively explain the weakening of the heterocyclic ether bond leading to accelerated and easier opening of the pyran ring in a flavonoid unit, as well as the facility with which hardening by autocondensation can occur. As in synthetic formaldehyde-based resins the same effect explains the decrease in energy of activation of the condensation of polyflavonoids with formaldehyde leading to exterior wood adhesives curing and hardening [69].

2. *Hardening by Autocondensation of Tannins*

The autocondensation reactions characteristic of polyflavonoid tannins have only recently been used to prepare adhesive polycondensates hardening in the absence of aldehydes [70]. This autocondensation reaction is based on the opening under alkaline and acid conditions of the O1–C2 bond of the flavonoid repeating unit and the subsequent condensation of the reactive center formed at C2 with the free C6 or C8 sites of a flavonoid unit on another tannin chain [70–74]. Although this reaction may lead to considerable increases in viscosity, gelling does not generally occur. However, gelling occurs when the reaction occurs (i) in the presence of small amounts of dissolved silica (silicic acid or silicate) catalyst and some other catalysts [70–75], and (ii) on a lignocellulosic surface [74]. In the case of the more reactive procyanidin and prodelphinidin type tannins, such as pine tannin, cellulose catalysis is more than enough to cause hardening and to produce boards of strength satisfying the relevant standards for interior-grade panels [74]. In the case of the less reactive tannins, such as mimosa and quebracho, the presence of a dissolved silica or silicate catalyst of some type is essential to achieve panel strength as required by the relevant standards. Autocondensation reactions have been shown to contribute considerably to the dry strength of wood panels bonded with tannins, but to be relatively inconsequential in contributing to the bonded panels' exterior-grade properties which are rather determined by polycondensation reactions with aldehydes [74–76]. Combinations of tannin autocondensation and reactions with aldehydes, and combinations of radical with ionic reactions have been used both to decrease the proportion of aldehyde hardener used as well as to decrease considerably more the already low formaldehyde emission yielded by the use of tannin adhesives [74–76].

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V. ANALYSIS

Various methods of analysis are available for the determination of tannin content. These methods can generally be grouped into two broad classes:

1. *Methods aimed at the determination of tannin material content in the extract*. The classical method of this type still used is the hide-power and derived methods. These methods were devised to determine which percentage of the extract would participate in leather tanning. The main drawback for their use for adhesives in their inability to detect and determine the approximate 3 to 6% of monoflavonoids and biflavonoids, or phenolic "nontannins," present in the extract which do not contribute to tanning capacity but which do definitely react with formaldehyde and contribute to adhesive preparation.
2. *Methods aimed at the determination of phenolic material present in the extract that can be reacted with formaldehyde*. These methods were devised particularly for tanning extracts used in adhesives and are all based on the determination of some of the products of reaction of the flavonoids with formaldehyde.

Accepted methods of the first type comprise the hide-power method [77], the refractometric method, and various visible, ultraviolet, and infrared spectrometric methods. Accepted methods of the second type include comparative methods such as the Stiasny–Orth method [78,79] and its modifications, all these being gravimetric methods largely obsolete today due to the lack of reliability consequent to coprecipitation of some carbohydrates together with the phenolic material of the tannin extract and to the results being expressed in an absolute value which is never reportable to a percentage of useful material in the extract, the Lemme [80] sodium bisulfite backtitration method, the ultraviolet spectrophotometric molybdate ion method [77,81], and infrared spectrophotometric methods [82].

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